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THE EFFECT OF IRON OXIDES ON THE PROPERTIES AND STRUCTURE OF GLAZED GLASSES

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The effect of iron oxides with a molar content of 2.5 to 35.0% (above 100%) on the properties of aluminoborosilicate glasses is investigated. The specifics of phase separation in iron-bearing glasses and their heat-treatment products and the kinetics of liquation processes are demonstrated. The valence-coordination state of iron ions and the effect of thermal treatment on this state are identified. The dependence of the physicochemical properties of glasses on their chemical composition and structure is considered. The possibility of making colored glaze coating with preset properties and textures is substantiated.

Among the pigment oxides used in glass technology, iron oxides attract the most attention. In some cases iron oxides are undesirable impurities imparting various shades to glass, and in other cases iron oxide is a component introduced in order to obtain glasses and coating with certain properties. The theoretical and practical interest in iron-bearing glasses is due to the following reasons: the presence of iron ions in two degrees of oxidation (Fe^{2+} and Fe^{3+}) and in different coordination states (4 or 6), the ability of iron oxides to impart valuable technical properties to glasses, and the possibility of using industrial waste and available materials to introduce iron oxide.

Clear glass compositions in the system $\text{Na}_2\text{O} - \text{CaO} - \text{B}_2\text{O}_3 - \text{Al}_2\text{O}_3 - \text{SiO}_2$ were selected as a basis for the synthesis of iron-bearing glazed glasses (% , here and elsewhere molar content): 7.5 – 10.0 Na_2O , 5.0 – 10.0 CaO , 10.0 – 15.0 B_2O_3 , 2.5 – 5.0 Al_2O_3 , and 65.0 – 70.0 SiO_2 . Iron oxides were introduced in an amount from 2.5 to 35.0% (above 100%) with a 2.5% interval for a content from 2.5 to 10.0% and a 5.0% interval for a higher content.

The melting temperature of iron-bearing glasses is 1350 – 1400°C. They have good technological properties and their color varies from light brown to black. The glass samples are x-ray-amorphous.

A relatively low melting temperature, an oxidizing gas medium, and an absence of natural oxidizers were the reason for the fact that iron in experimental glasses mainly exists in the highest degree of oxidation. The ratio of Fe_2O_3 : ($\text{FeO} + \text{Fe}_2\text{O}_3$) varies within a range of 0.93 – 0.97 depending on the composition and grows as the Fe_2O_3 content in the initial batch increases. Particular contents of FeO and Fe_2O_3 in glasses were determined according to the method in [1].

The crystallization capacity of the glasses was determined using the gradient crystallization method within a temperature interval of 500 – 1100°C and subsequent identification of the phase composition employing an x-ray diffractometer. Thermal treatment of glass samples containing 2.5 – 10.0% Fe_2O_3 does not lead to their crystallization. An increase in Fe_2O_3 content up to 15% results in surface crystallization in the form of a thin crystalline film, whose phase composition, due to its insignificant quantity, cannot be identified by x-ray phase analysis. With a content of Fe_2O_3 equal to 20 – 35%, volume crystallization of samples is registered. The main crystalline phase is magnetite $\text{Fe}^{2+}\text{Fe}_2^{3+}\text{O}_4$ and there are traces of hematite $\alpha\text{-Fe}_2\text{O}_3$. The high crystallization capacity of iron-bearing glasses is due to the formation of nonsilicate phases, which do not contain polyanions and, therefore, have low energy of activation of the crystallization process.

Differential thermal analysis revealed the presence of endothermic effects on thermograms in the temperature range of 515 – 710°C related to the glass-softening processes. The type of endothermic effects having double minimums is evidence of liquation phenomena in glasses. The slight exothermic effect with a maximum at 340°C on thermograms of glasses containing at least 15% Fe_2O_3 is presumably due to the oxidation of magnetite, whereas the second exothermic effect with a maximum at 825 – 838°C is due to the oxidation of residual magnetite caused by diffusion of oxygen via the surface film, which becomes more porous at a high temperature. The low-intensity exothermic effect at 960 – 990°C is related to the crystallization of iron-bearing compounds.

The introduction of iron oxide into a composition of aluminoborosilicate glass intensifies liquation phase separation: as the content of Fe_2O_3 increases, the size of liquation

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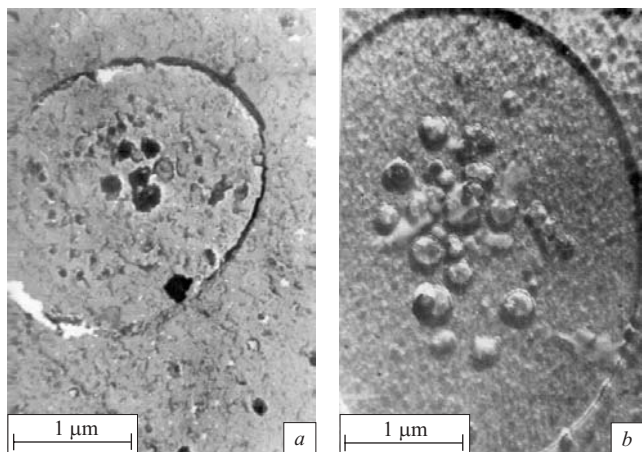


Fig. 1. Electron microscope photos of glasses heat-treated at 770°C for 48 h of composition $7.5\text{Na}_2\text{O} \cdot 5\text{CaO} \cdot 15\text{B}_2\text{O}_3 \cdot 2.5\text{Al}_2\text{O}_3 \cdot 70\text{SiO}_2$ with additives (above 100%) of 10% (a) and 15% (b) Fe_2O_3 .

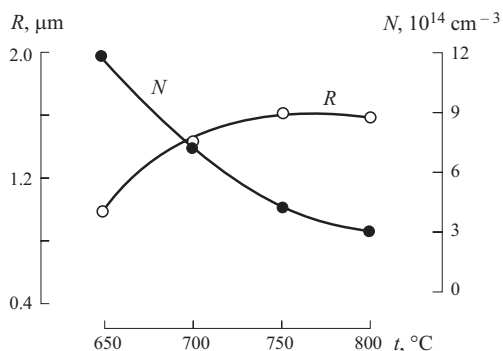


Fig. 2. Dependence of the mean drop radius R and total number of drops per volume unit of glass N on temperature of thermal treatment lasting 24 h.

drops grows and the quantity of drops per volume unit increases.

Local x-ray spectral analysis of elemental compositions of the drop phase and the matrix phase was carried out using an electron microprobe. Drops sized 4–5 μm were grown in glass samples under protracted heat treatment (48 h) at a temperature of $770 \pm 20^\circ\text{C}$ (Fig. 1). It has been established that the quantity of SiO_2 in the glass matrix is 53% higher than in the drop phase and the content of Na_2O is 32% lower than in drops. The amount of CaO is slightly higher in drops. As for iron oxide, it is predominantly concentrated in the drop phase, which presumably brings its composition closer to the composition of future crystalline formations.

The liquation structure morphology and kinetics of its evolution were studied based on variations in the mean radius of liquation drops and their number per volume unit under thermal treatment of samples. Phase disintegration occurs already during cooling of the glass melt. The liquation drop structure typical of initial iron-bearing glasses persists under heat treatment up to 750°C, growth and fusion of sin-

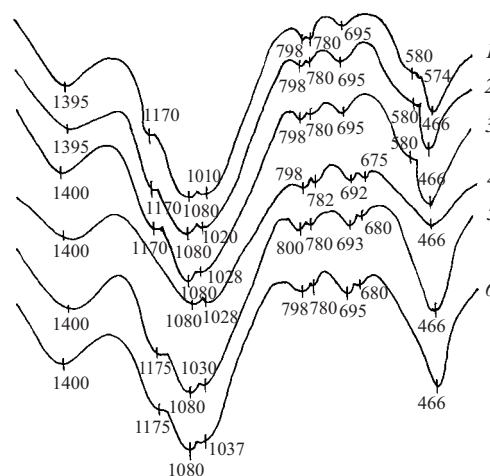


Fig. 3. IR spectra of glasses of composition $10\text{Na}_2\text{O} \cdot 10\text{CaO} \cdot 15\text{B}_2\text{O}_3 \cdot 2.5\text{Al}_2\text{O}_3 \cdot 62.5\text{SiO}_2$ with additives (above 100%): 2.5% (1), 5.0% (2), 7.0% (3), 10.0% (4), 20.0% (5), and 35.0% (6) Fe_2O_3 .

gle drops is registered in a temperature interval of 750–850°C, and a two-skeleton liquation structure is formed at a temperature of 900°C. Crystals with a regular hexagonal shape and clearly defined facets emerge within a temperature interval of 900–950°C. Thus, iron-bearing glasses of the considered system in initial stages are characterized by drop liquation, which under heat treatment transforms into a two-skeleton type of liquation.

The kinetics of liquation phase separation in early stages of heat treatment can be estimated by reaching an equilibrium state, which is characterized by constant volumes of the coexistent phases. It is established that the drop-phase volume relatively rapidly reaches an equilibrium in the considered glass, i.e., in 4 h.

Figure 2 shows the temperature dependences of the mean radius variation of liquation drops and their number per volume unit for a constant duration of heat treatment. The total number of heterogeneous sites per volume unit decreases with increasing temperature, and the mean particle radius increases, reaching a certain maximum value at a temperature of 750°C.

The introduction of Fe_2O_3 into glasses of the system $\text{Na}_2\text{O} - \text{CaO} - \text{B}_2\text{O}_3 - \text{Al}_2\text{O}_3 - \text{SiO}_2$ significantly lowers the liquation temperature and the rate of formation of liquation heterogeneities and increases their quantity per volume unit and the mean particle radius.

The introduction of iron oxide into three-component and polycomponent glasses causes changes in the silicate and borate structural components: iron-oxygen tetrahedral groups $[\text{Fe}^{3+}\text{O}_4]$ are formed and incorporate into the silicon-oxygen skeleton, the number of boron-oxygen tetrahedral groups $[\text{BO}_4]$ decreases and the number of trigonal groups $[\text{BO}_3]$ increases, etc. [2, 3]. Structural changes occurring in the considered glasses as their content of iron oxides increases were

investigated using spectroscopic methods. IR spectroscopy and nuclear magnetic resonance (NMR).

The IR spectra of iron-containing glasses have clearly expressed bands in ranges of 1400, 1080–1100, 780–800, 675–695, and 465–470 cm^{-1} (Fig. 3). Identification of groups $[\text{BO}_4]$ in aluminoborosilicate glasses, in which groups $[\text{SiO}_4]$ are present, is difficult. This is due to the fact that the intense absorption range correlating with boron in a tetrahedral coordination is shifted toward lower frequencies, where vibrations of groups $[\text{SiO}_4]$ are manifested. The specifics of the IR spectra of the considered glass include a shift of the main absorption band maximum in the range of 900–1100 cm^{-1} from 1037 to 1010 cm^{-1} and a decrease in its intensity with increasing iron content. This may be related to a decreased degree of polymerization of tetrahedral groups $[\text{SiO}_4]$ and an increased degree of differentiation of structural complex types. The emergence of low-intensity maximums in a range of 574–580 cm^{-1} may be evidence [2] of atom vibrations in Fe^{3+} –O bonds in polymerized tetrahedrons $[\text{FeO}_4]$.

The valence-coordination state of iron ions was identified more precisely using the NMR method otherwise known as the Mössbauer effect. Initial iron-bearing glasses and products of their heat treatment were investigated.

The coordination state of Fe^{3+} in the considered glasses is determined by the molar ratio of $(\text{Na}_2\text{O} + \text{CaO}) : (\text{Al}_2\text{O}_3 + \text{B}_2\text{O}_3 + \text{Fe}_2\text{O}_3)$, where Na_2O and CaO are donors of oxygen. With an excess of $(\text{R}_2\text{O} + \text{RO})$, iron ions, as well as aluminum and boron ions, form tetrahedral oxygen complexes $(\text{Fe}^{3+}\text{O}_{4/2})^-\text{Na}^+$ and $(\text{Fe}^{3+}\text{O}_{4/2})^-\text{Ca}^{2+}$ and replace silicon in the glass structure, i.e., compositions with the ratio of $(\text{Na}_2\text{O} + \text{CaO}) : (\text{Al}_2\text{O}_3 + \text{B}_2\text{O}_3 + \text{Fe}_2\text{O}_3) > 1$ typically have a tetrahedral coordination for Fe^{3+} and an octahedral one for Fe^{2+} . Glasses with a ratio of $(\text{Na}_2\text{O} + \text{CaO}) : (\text{Al}_2\text{O}_3 + \text{B}_2\text{O}_3 + \text{Fe}_2\text{O}_3) < 1$ exhibit an isometric shift of spectra, which is due to the presence of Fe^{3+} ions in the octahedral coordination in glass. In the latter case, tetrahedral aluminum and boron polyhedrons are presumably constructed first, and the remaining oxygen participates in the formation of iron-oxygen tetrahedrons. A prevailing part of the iron ions in this case exists in a six-coordination state and makes part of the drop phase that is rich in iron, in which hematite intensely crystallizes under heat treatment.

According to NMR data, heat treatment of glasses leads to oxidation of bivalent iron to trivalent, which forms groups $[\text{Fe}^{3+}\text{O}_6]$. The ferromagnetic phase (magnetite Fe_3O_4) that is present in glasses containing over 7.5% iron oxides in heat treatment transforms into hematite. The maximum quantity of Fe_3O_4 uniquely depends on the content of Fe^{2+} and Fe^{3+} ions existing in the position of modifiers. Formation of hematite is possible only in glasses with a low content of Fe^{2+} , as happens in glasses in which $\text{Fe}_2\text{O}_3 : (\text{FeO} + \text{Fe}_2\text{O}_3)$ is equal to 0.93–0.97.

Studies of the physicochemical properties of glasses were carried out for the purpose of estimating the effect of

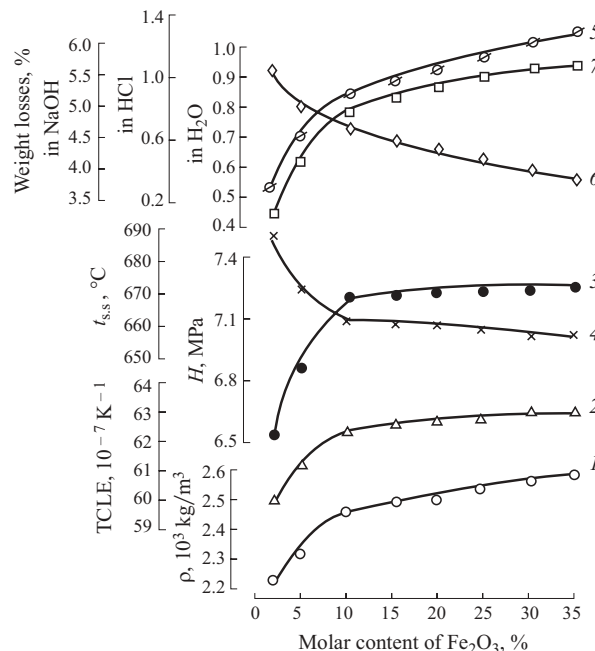


Fig. 4. Dependence of physicochemical properties of glasses in the system $\text{Na}_2\text{O} - \text{CaO} - \text{B}_2\text{O}_3 - \text{Al}_2\text{O}_3 - \text{Fe}_2\text{O}_3 - \text{SiO}_2$ on Fe_2O_3 content (above 100%): 1) density; 2) TCLE; 3) microhardness; 4) softening start temperature; 5, 6, and 7) glass weight losses in H_2O , 1 N NaOH, and 1 N HCl, respectively.

Fe_2O_3 on glass parameters. The viscosity of glasses with up to 10% Fe_2O_3 additive within the softening interval varies insignificantly with increasing content of iron oxides. A further increase in the content of Fe_2O_3 decreases low-temperature viscosity. The effect of iron oxides on glass viscosity is due to the formation of various structural groups of iron. Thus, on incorporation of groups $[\text{Fe}^{3+}\text{O}_4]$, the glass skeleton loosens due to the larger sizes of these groups compared with $[\text{SiO}_4]$ groups: their interatomic distances Si–O and Fe–O are, respectively, 0.161 and 0.187 nm [4]. This causes an insignificant decrease in viscosity. As the quantity of Fe_2O_3 grows, accumulation of $[\text{Fe}^{3+}\text{O}_6]$ groups is registered and iron ions act as modifiers, which weakens the structural lattice and contributes to a more significant decrease in viscosity.

Upon introducing up to 15% iron oxides in glasses, the glass density intensely grows and amounts to $(2.44 - 2.57) \times 10^3 \text{ kg/m}^3$, which is quite expected, since the atomic mass of iron is large (55.84). A further increase in the quantity of iron oxides in glass causes a less significant increase in density; accordingly, an inflection is seen in the composition–density curve (Fig. 4). The change in the course of this dependence is presumably related to the change in the coordination state of the iron ions.

Iron oxides do not have a perceptible effect on the TCLE of the glasses considered, which is due to a small increase in the average bond energy in formation of a mixed iron-silicon-oxygen skeleton. On introducing Fe_2O_3 , the relative share of $[\text{SiO}_4]$ tetrahedrons in the mixed skeleton drops [5],

since each Fe_2O_3 molecule forms two tetrahedral groups $[\text{Fe}^{3+}\text{O}_4]$. At the same time, the concentration of strong covalent $\text{Si}-\text{O}$ bonds in the skeleton decreases and the quantity of the more ionic and less strong $\text{Fe}^{3+}-\text{O}$ bond grows. Due to the development of the structural skeleton at the expense of iron-oxygen tetrahedrons, the TCLE of glasses grows to some extent on introducing up to 10% Fe_2O_3 . This growth is less significant on a further increase in the iron oxide content. The TCLE of glasses is within the limits of $(61.6 - 63.1) \times 10^{-7} \text{ K}^{-1}$.

The microhardness of the experimental glasses monotonically grows with increasing content of iron oxides in the glass. An increase in the total quantity of tetrahedral groups in the glass upon introducing 5 – 10% Fe_2O_3 is manifested in growing microhardness. Accumulation of six-coordination iron and an increasing concentration of iron ions is accompanied by a decrease in the degree of cohesion of the structural skeleton of the glass and a certain weakening of bonds, as a consequence of which the course of the curve reflecting microhardness versus the quantity of Fe_2O_3 changes.

The introduction of Fe_2O_3 into initial glass compositions decreases water resistance; the most significant weight losses are registered when boiling in water samples with additives of 5 and 10% Fe_2O_3 . The shape of the curve characterizing acid resistance of iron-bearing glasses is similar. A decrease in water and acid resistance of glasses with increasing content of Fe_2O_3 can be interpreted as follows. The process of depolymerization of the silicon-oxygen lattice intensifies as the concentration of iron ions increases, which enhances the solubility of vitreous material in acids [6]. Certain retardation of the process of glass destruction containing over 10% Fe_2O_3 under the effect of water and acid is presumably related to localization of Na^+ and Ca^{2+} ions in structural complexes containing iron ions, where they are fixed more strongly than in non-bridged bonds $\text{Si}-\text{O}\dots\text{Na}^+$.

It is known that alkali resistance of glasses is characterized by interaction of alkali solutions directly with the vitreous skeleton, destruction of the latter, and transition of resulting anions into the alkali solutions. The principal role in the considered glasses is played not by the quantity of introduced Fe_2O_3 but by the content of SiO_2 . As the "acidity" of the skeleton decreases, i.e., the relative share of $[\text{SiO}_4]$ tetrahedrons becomes lower, the specified interaction becomes weaker and alkaline resistance grows.

Thus, the physicochemical properties of glasses depend on the valence-coordination state of iron ions and their position in the glass structure, which corroborates the structural

role of Fe^{3+} identified by spectroscopic methods. The effect of Fe^{2+} ions on glass properties is not so significant due to their low concentration.

To establish the possibility of producing high-quality colored coatings, glaze suspensions based on iron-bearing glasses, which did not crystallize within the temperature gradient, were deposited on a ceramic substrate with subsequent firing within a temperature interval of 700 – 1100°C and exposure at the maximum temperature for 30 min and 1.5 h.

The glasses containing 5% iron oxide (above 100%) in firing form a light brown semitransparent coating; with an Fe_2O_3 content equal to 10%, the coating becomes brown with a reddish tint, and increasing Fe_2O_3 content to 15% produces dark brown glazes. Fusion of a glazed glass containing 25% iron oxides produces a dull coating with surface defects: blisters and numerous pinholes. The optimum temperature interval for coating fusion is 910 – 950°C. The best decorative properties are observed in glazes with a content of iron oxides equal to 5 – 15%, which ensures the formation of a semitransparent coating with a mirror-like luster and good spreading. An increase in the heat treatment duration improves the spreading and luster of the coating without modifying the color parameters of the glaze layer and decreases the number of pinholes.

The TCLE of glaze coatings within a temperature interval of 20 – 400°C is equal to $(54 - 63) \times 10^{-7} \text{ K}^{-1}$, which provides for good coordination of coatings with ceramic substrates and high thermal resistance, i.e., more than 200°C.

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